

Investigating Charge Transport in Molecular Switches with Neural Networks

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ABSTRACT: The control of charge transport on a polymer chain by impurity molecules working as switches is studied. Charge propagation is estimated using a backpropagation neural network approach. The supervised learning is accomplished using theoretical results in which the chain is modeled by a tight-binding Hamiltonian extended to include the effects of an external electric field. The charge transport through the sites that work like a switch is analyzed by the numerical integration of the equations of motion. For a donor–acceptor pair of impurities, we found that the chain offers a wide range of devices, from simple switches to perfect molecular rectifiers. The influence of the parameters of the molecules on the charge transport, the role of the length of separation between the sites where the impurity molecules bond, as well as the changes they must undergo to characterize each kind of molecular switch are determined. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 1060–1066, 1999

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Introduction

Molecular electronics is emerging as a promising field of research and a powerful source of technology.^{1–6} The manipulation of sin-

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gle molecules opens the possibility of creation of a wide range of functional devices that mimic the solid-state ones, and may also have other new and important characteristics and functions. The fabrication of molecular electronic devices is not so far in the future and we can already foresee and even design various special molecules.^{7,8}

Conducting polymers are a fundamental part of molecular devices. They can work as molecular level wires linking and carrying charge through the molecular circuit.⁹ In this sense, polyacetylene has appeared early as a good candidate to integrate molecular switches. One of its ways of conducting charges, through bond order solitons,^{10,11}

is a quality of much interest, and could be used to create molecular switches. Impurities and doping radicals can work as pinning centers and barriers to the solitons. Bistable impurities can also work as switches by allowing or denying the passage of moving charged solitons through a certain region of the chain.¹²

The main purpose of the present work is to establish the basic character of radicals that must be bonded to a polyacetylene chain to create molecular switches. Doping molecules are introduced as a means of altering polymer conduction properties, controlling the charge transfer throughout the chain. The determination of an optimum molecular switch, by varying the parameters of the doping molecules, is accomplished. The dynamics of charged solitons propagating on the polyacetylene chain is studied through numerical solution of the equations of motion for the electronic and lattice degrees of freedom of the system. A model tight-binding Hamiltonian is modified to include an external electric field and short-ranged site-type impurity potentials to represent the radicals bonded to the main chain. Actually, we determine the possibility of a charged moving soliton crossing the region in which the radicals are added. We verified that the solitons can pass away, be trapped, or reflect on this region, depending on the configuration of the radicals.

Neural networks (NNs) have become powerful tools for researchers in recent years.¹³ Problems of classification, modeling, mapping, association, and dynamical processes can be handled very well, frequently giving better results than other conventional techniques. Use of NNs in computational chemistry has been shown to solve a wide range of problems.^{14,15}

Neural networks are computer programs in which the role of neurons is played by processing elements (PEs) that are connected in a net and can receive and transmit information among themselves. All information received by one PE is processed with the addition of a transfer function and then transferred to other PEs. Communication between PEs is mediated by weights that work very much like the actual synapses between neurons. It is the modification of these weights that enables the network to learn and execute the tasks it is meant to perform.

In this work, we use the backpropagation method of supervised learning to train a neural network to determine the final outcome of the numerical simulation of the propagation of a charged soliton through the switching sites. In the

training phase, the input set for the polymer includes the site energies and the bonding sites for each radical and bonding-site separation. Of course, other representations are possible, but this choice yields a good learning rate and a prediction rate that seems reasonable. Using the trained network we generate phase diagrams covering all relevant cases for the radical parameters. The advantage of using neural networks is that thousands of final outcome calculations can be done without prohibiting computational implications.

This article is organized as follows. In the next section we present the model and a brief description of the simulation method. We discuss the results of the theoretical calculations. We then provide a brief review of the backpropagation method and describe the network architecture used. The following section is devoted to the application of the backpropagation method to model the simulations. Finally, we provide a summary and concluding remarks.

Model and Formalism

We express the Hamiltonian describing the chain with impurities as:

$$H = - \sum_{n,s} (t_{n,n+1} C_{n+1,s}^\dagger C_{n,s} + H.C) + \sum_n \frac{K}{2} (u_{n+1} - u_n)^2 + \sum_n \frac{M}{2} \dot{u}_n^2 + \sum_{p,s} V_p (C_{p,s}^\dagger C_{p,s}) \quad (1)$$

with:

$$t_{n,n+1} = e^{+i\gamma A} [t_0 - \alpha(u_{n+1} - u_n)] \quad (2)$$

Here, H is an SSH-type Hamiltonian,¹⁰ modified to include the electric field and the impurities parameters. $C_{n,s}$ is the annihilation operator of a π electron with spin s at the n th lattice site, u_n is the displacement coordinate of the n th CH group, t_0 is the transfer integral between the nearest-neighbor sites in the undimerized chains, α is the electron-phonon coupling, M is the mass of a CH group, K is the spring constant of a σ -bond, and V_p is the strength of an impurity located in the p th site. Also, $\gamma \equiv ea/(\hbar c)$, with e being the absolute value of the electronic charge, a the lattice constant, and c the light velocity. The relation between the time-dependent vector potential, A , and the uniform electric field, E , is given by $E = -\frac{1}{c}\dot{A}$.

We prepare initially a stationary state, which is fully self-consistent with respect to both degrees of freedom, of the electrons and phonons, as the initial conditions of the calculations.¹⁶ We obtain an equilibrium dimerization, $u_0 = 0.04 \text{ \AA}$, in accordance with the SSH model.¹⁰ Then, under the action of the electric field, the electronic and the lattice equations of motion are numerically integrated. The electric field is applied from $t = 0$ to $t = t_{\text{off}}$, a timespan necessary for the charged soliton to acquire a velocity close to its maximum possible value.¹⁷ We use $t_{\text{off}} = 60 \text{ fs}$ and $|E| = 0.025E_0$, with $E_0 = \hbar\omega_Q/(ea)$. Therefore, the soliton is moving at a constant velocity when it reaches the switching sites and the electric field is turned off.

We use, as parameters, the commonly accepted values for polyacetylene: $t_0 = 2.5 \text{ eV}$, $K = 21 \text{ eV \AA}^{-2}$, $\alpha = 4.1 \text{ eV \AA}^{-1}$, and $a = 1.22 \text{ \AA}$, and for the impurity potentials we take V_p ranging from 10^{-3} to $0.2t_0$. Periodic boundary conditions are assumed for the electronic wave functions, $\Psi_{k,s}$, and the lattice displacements, u_n —for we want to simulate very long polyacetylene chains and we are not concerned with the end effects.^{10,16}

In this study, the total number of lattice points on the chain is $N = 101$, thus allowing the presence of a soliton on the chain. The total number of electrons on the chain (Ne) is 100 in all cases, which means that, in the initial condition, we have a positively charged soliton on the chain.

Each of these simulations takes 2 hours of CPU time on a DEC Alpha-400 workstation.

Dynamical Simulation Results

We performed 419 simulations. One single positively charged soliton is initially present at around site 20. Two different radical molecules are bound to different positions on the chain in each case. Figure 1 shows very schematically the initial configuration of the polymer chain.

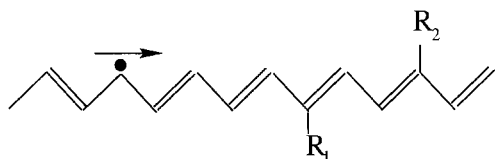


FIGURE 1. Schematic representation of a moving charged soliton on polyacetylene and the bonding radicals that work as a switch.

The solitons of polyacetylene have the very interesting property of accumulating charge around the topological defect of the bond order pattern only on even or odd sites. This soliton character has important consequences on the switching mechanism. In this work, we call solitons that accumulate charge on even (odd) numbered sites "even (odd) solitons."

Besides the parity of the soliton (charge on even or odd sites), the position on the chain where the radicals bond, and the consequent alteration of the CH unit site energy, play a fundamental role in the switching process. Therefore, we systematically change the bonding sites and the radical parameters. For each configuration we made the moving charged soliton go through the chain.

Subtle changes in the intensity of the radicals have proven to lead to very different results. The order of appearance of the donor and acceptor radicals in the soliton path, as well as the parity (even or odd) of the sites where they bond, is also fundamental for the charge propagation on the chain. The charged soliton can move forward, be trapped, or reflect on the switching sites, depending on their arrangement and the parity of the soliton.

There is an overall pattern observed in the extensive number of cases studied: As the radical intensity gets bigger than a given threshold, the soliton gets trapped, or is reflected by the switch.

In the impurity separation and impurity intensity graphics one can distinguish three different charge transporting phases. Each line separates radical configurations, allowing passing, reflecting, or trapping of the soliton. Therefore, there exist three different phases: phase I contains configurations allowing the soliton passage; phase II represents configurations where the solitons get trapped; and in phase III the solitons reaching the switch are reflected.

Backpropagation Method and Network Architecture

Here we present a brief discussion of the method. The backpropagation of errors is a learning method (i.e., a method for the correction of weights).¹⁸ The great appeal of this method comes from an explicit and well-defined set of equations for the correction of the weights. The equations are applied to the correction of the weights in the last layer and then to the previous layers up to the

first. This supervised learning process utilizes pairs of input–output data. These pairs are sets of real variables in which we initially associate a known output for each given input. At the beginning the weight values are set at random. The correction in this method is based on the difference between the actual response of the net and the desired output, and follows the gradient-descent method.¹⁹

We use normalized data to prevent numerical calculation problems. Upon repeatedly presenting the input and desired output sets to the network the weights are gradually corrected until the response and the desired output agree to some extent. This is accomplished by calculating the root-mean-square error between them until it becomes smaller than 10^{-3} for the training set.

In our network architecture each layer of neurons is fully connected to the layer below it (Fig. 2). We considered nets with several configurations and found that the best results were given by a four-layer network. The input layer has six PEs. Five PEs make up the system: the two radical bonding site parities; the two radical site energies; and the radical separation length, respectively. The sixth PE is a bias. The hidden layers consist of eight PEs: seven active PEs and a bias. The biases are introduced to formally account for the parameters of the transfer functions inherent to artificial neurons. Finally, the output layer has only one PE, giving the final position of the soliton after interaction with the switching sites.

From the 419 simulations, we used 385 sets of input–output to train the network. The rest were

used as a control set. After training, the recall rate (i.e., the performance of the net in recognizing the training set) was about 100% if we look at the classes of results—that is, get trapped, pass through, or reflect at the switching sites. The correctness of values given to the control set and prediction rate was at the 99% level.

Neural Network Results

Using the trained network we generated 9702 cases. The input sets that represent the impurity strengths, signs, parities, and separation have been generated in their respective ranges of interest.²⁰ It is important to note that all these values are in the intervals expanded by the dynamical simulations and no extrapolation was done.

Figure 3 presents the more compelling results, namely when both impurities bond at sites with the same parity as the soliton. The four quadrants of each graph represent donor–acceptor pair when the signs of the impurities are different and pairs of donor–donor or acceptor–acceptor for the case of equal signs. We observe a steep change in the soliton behavior for small impurity separations (two to four sites apart). There is no qualitative change of behavior with the separation from four to eight sites (half the soliton width). The separation between phases is also clear; that is, soliton passage (phase I), trapping (phase II), and reflection (phase III).

In Figure 4, we focus on the special case of the diagonals of Figure 3. The dependence on impurities separation and intensity is plotted. Although there are some results for the diagonal that represents donor–acceptor pairs and the other diagonal, representing pairs of donors or acceptors, is also shown. Indeed, the more complex behavior is presented by the donor–acceptor pair (Fig. 4a). Nevertheless, one can induce the same change of behavior, from passage to trapping to reflection, through a small change in the impurity strength. Therefore, the control of soliton behavior that matters for molecular electronics is possible to achieve with the two kinds of impurity addition (donor–acceptor pairs and donor or acceptor pairs).

The cases in which the impurities bond at sites of different parity are presented in figures provided as “supplementary material.” The two figures are actually different, because the order of appearance of the impurities in the soliton path matters. The difference is due to the asymmetrical

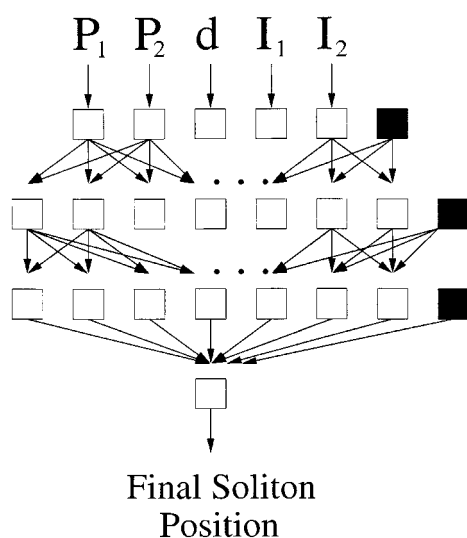


FIGURE 2. Schematic representation of the neural network architecture used in this work.

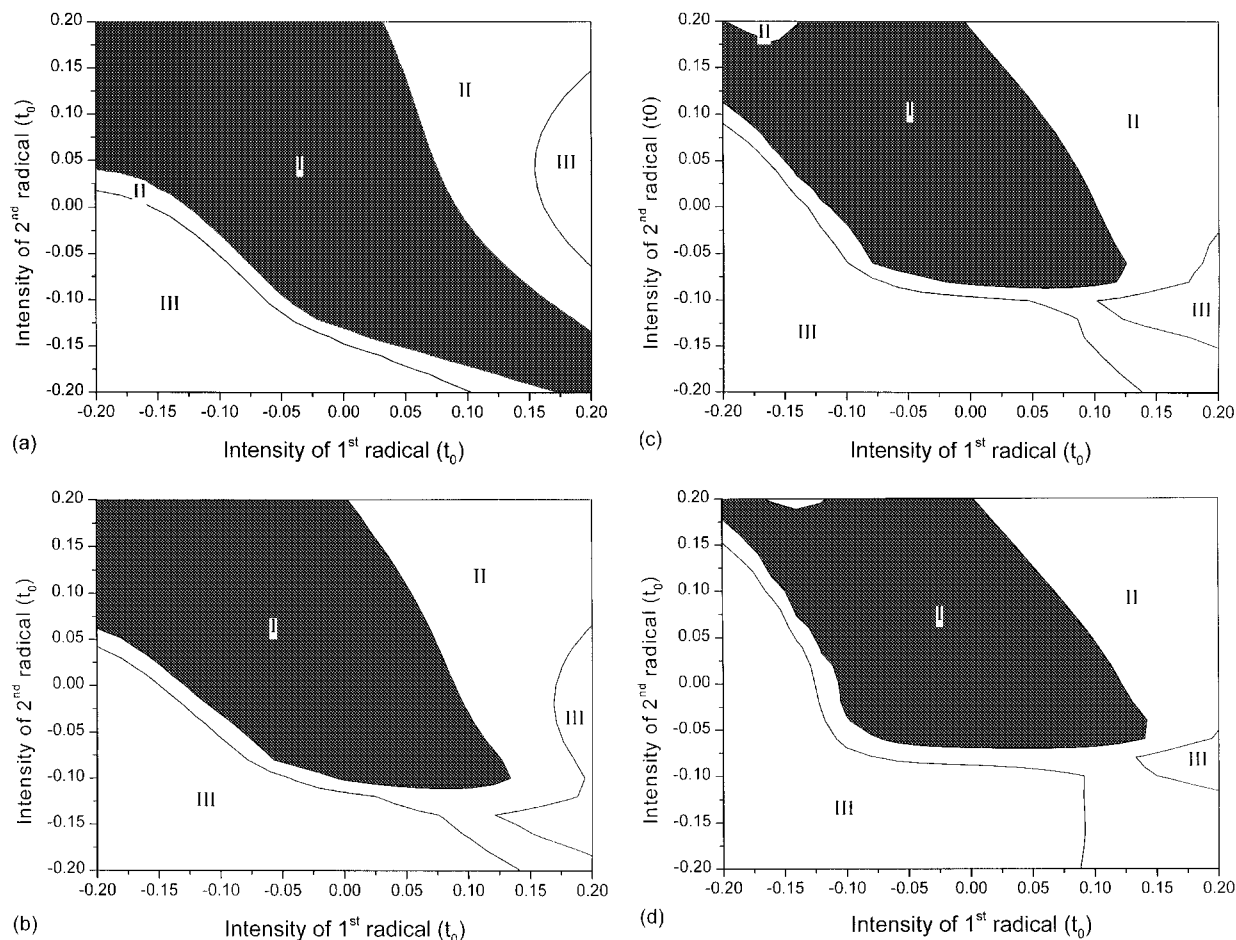


FIGURE 3. Charge propagation phase diagrams for a polyacetylene chain with a pair of radicals bonded at sites with the same parity of the soliton. Phase I: configurations that allow the passage of a soliton; phase II: configurations that trap the soliton; phase III: configurations that reflect the soliton. (a) Radicals bonded two sites apart. (b) Radicals bonded four sites apart. (c) Radicals bonded six sites apart. (d) Radicals bonded eight sites apart.

effective potentials encountered by the soliton associated with each impurity.²¹ In these cases, the soliton behavior can again be controlled by small changes in the intensity of one of the impurities.

Discussion and Summary

The propagation of a moving charged soliton on a single polyacetylene chain, where radical molecules work as a switch, has been investigated. This study was carried out by numerical calculations using an extended version of the SSH model and neural network interpolation.

The switching molecules are modeled by the changes they exert on the energy of the polyacetylene site where they bond.

The soliton passage, reflection, or trapping on the switch was investigated for a large number of configurations of bonding molecules. Changes in the bonding site positions and site energies were carried out and the characteristics of the various switches were analyzed.

We verified that the molecular switches on polyacetylene are very sensitive to the parity of the charged soliton and, consequently, to the parity of the radical bonding sites. The same pair of donor-acceptor bonding radicals can be irrelevant or an insurmountable obstacle to a given soliton. The passage depends on the parity of the sites at which the radicals bond, the impurity intensities, their order of appearance, and the parity of the soliton and its charge sign. It should be noted that the introduction of a Coulomb interaction in the

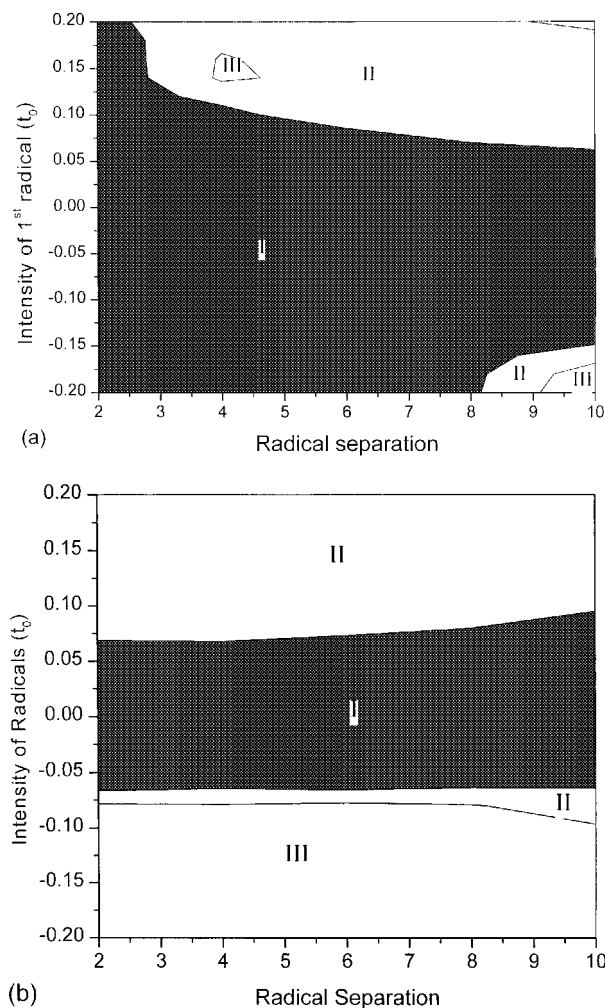


FIGURE 4. Charge propagation phase diagrams for a polyacetylene chain with a pair of radicals of same intensity modulus bonded at sites with the same parity of soliton. The phases are the same as in Figure 3. (a) Donor-acceptor pair. (b) Donor-donor or acceptor-acceptor pair.

SSH model leads to the appearance of soliton charge on the even and odd sites. Moreover, there is a small change in the effective potential around the impurity sites. However, as shown in ref. 21, the inclusion of this kind of interaction does not change the qualitative behavior of the phase diagrams presented in the current work.

We found that the subtle soliton behavior dependence on the impurity separation can be accomplished by avoidance of bonding the impurities too close together. This is particularly applicable to the design of molecular circuits. Therefore, the specific characteristics of each switch can be controlled by a small change in only one of the

impurity strengths. The choice of which impurity to control and how much one should change the impurity strength can be done using the results shown in Figure 3 and also the figures included in the "supplementary material." We are presently combining *ab initio* and parametric calculations to determine how the impurity strength of a given radical could be estimated and how this impurity strength is related to the chemical structure of the radical bonded to the polymer chain.

In all simulations, the solitons move at a velocity close to maximal possible value and the electric field is turned off. In the presence of a continuous electric field, reflection by an impurity would essentially mean trapping, as the electric field will push the soliton back to the impurity sites. Weaker electric fields take long to accelerate solitons to maximum speed, thus leading to an increase in the number of trappings.

We have seen that radical molecules bonded to the polyacetylene chain can work as molecular switches. It is not necessary to add impurity molecules to the chain backbone. However, the addition of impurities to the body of the polymer chain could bring forth interesting new features to the switches.

The present model does not consider any change in the pattern of single-double bonds on the polyacetylene chain prior to soliton passage. The bonding radicals did not alter this pattern between their bonding sites. Therefore, the structural change on the single-double configuration between the radicals is not indispensable to the switching function.

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